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VYSOKÉ UČENÍ TECHNICKÉ V BRNĚ

FACULTY OF ELECTRICAL ENGINEERING AND COMMUNICATION

FAKULTA ELEKTROTECHNIKY
A KOMUNIKAČNÍCH TECHNOLOGIÍ

DEPARTMENT OF FOREIGN LANGUAGES

ÚSTAV JAZYKŮ

TECHNOLOGIES FOR STORING ELECTRICAL ENERGY IN ELECTRIC VEHICLES

TECHNOLOGIE PRO USKLADNĚNÍ ELEKTRICKÉ ENERGIE V ELEKTRICKÝCH VOZIDLECH

BACHELOR'S THESIS
BAKALÁŘSKÁ PRÁCE

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FAKULTA ELEKTROTECHNIKY A KOMUNIKAČNÍCH TECHNOLOGIÍ

Bakalářská práce

bakalářský studijní obor **Angličtina v elektrotechnice a informatice**
Ústav jazyků

Student: Marek Zdražil ***ID:*** 152325
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NÁZEV TÉMATU:

Technologie pro uskladnění elektrické energie v elektrických vozidlech

POKYNY PRO VYPRACOVÁNÍ:

V současné době je rozvíjejícím se trendem v dopravě elektromobilita, ať už plná, nebo částečná (hybridní elektromobily).
Vypracujte rešerši na téma systémů pro ukládání energie v elektrických vozidlech. Rozveďte technologie s perspektivou do budoucna a možné směry dalšího
vývoje.Věnujte se i problematice elektromobilů a elektromobility obecně, shrňte historii, problémy, současnost a perspektivy

DOPORUČENÁ LITERATURA:

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Inc., U.S. Department of Energy, Office of Fossil Energy, National Energy

Technology Laboratory

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Vedoucí práce: Mgr. Petra Langerová
Konzultant bakalářské práce: Ing. Jiří Tichý

doc. PhDr. Milena Krhutová, Ph.D., *předseda oborové rady*

ABSTRACT

This bachelors thesis is focused on technologies used for storing electric energy in electric vehicles. The first chapter deals with history of technologies for electric energy storing and their use in early electric vehicles. It continues by description of electric vehicles that were occasionally produced through the 20th century, up to 1990s when this technology became attractive again. The following chapter describes types of electric cars and gives us examples of currently produced cars. The third part deals with technologies used in present and recent past. Subsequently, in the last chapter, there are introduced technologies which might be sufficient substitution to current systems or even to conventional combustion engines in future.

ABSTRAKT

Tato bakalářská práce je zaměřena na technologie pro ukládání elektrické energie, s důrazem na jejich použití v elektrických vozidlech. První kapitola se zabývá historickým vývojem technologií pro ukládání elektrické energie a jejich použitím v prvních elektrických vozidlech. Dále popisuje elektrická vozidla, která byla sporadicky vyráběna v průběhu dvacátého století, až po devadesátá léta, kdy tato technologie opět nabyla na atraktivitě. V další části nalezneme rozdělení současných elektromobilů a zástupce těchto kategorií mezi automobily vyráběnými v současnosti. Třetí část se věnuje technologiím používaným v současnosti, či nedávné minulosti. Následně je uveden přehled technologií, které by mohly do budoucna nahradit současné systémy, nebo dokonce konvenční spalovací motory.

KEYWORDS

Electric vehicles, hybrid electric vehicles, Prius, Tesla S, Leaf, lead-acid, lithium-ion, lithium-polymer, Fuel cell, Flow cell, supercapacitor, lithium-sulphur, redox battery, silicone anode

KLÍČOVÁ SLOVA

Elektrická vozidla, hybridní vozidla, Prius, Tesla S, Leaf, olověné akumulátory, lithium-ion, lithium-polymer, palivový článek, Flow cell, superkondenzátor, lithium-síra, redoxní baterie, křemíková anoda

PROHLÁŠENÍ

Prohlašuji, že svou bakalářskou práci na téma Technologie pro ukládání elektrické energie v elektrických vozidlech jsem vypracoval samostatně pod vedením vedoucího a konzultanta semestrální práce a s použitím odborné literatury a dalších informačních zdrojů, které jsou všechny citovány v práci a uvedeny v seznamu literatury na konci práce.

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V Brně dne .... …...............................…

(podpis autora)

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1. INTRODUCTION

In the recent years, electro-mobility, as a way of transport using vehicles with electric drive, has become a fast growing area of transport and industry. There are many reasons why. One important reason is that developed countries are trying to decrease environment pollution in densely populated areas by decreasing amount of exhaust fumes. Other reason is linked to world reserves of fossil fuels. Since they are not infinite, lack of oil would have enormous effect on transport. Setting free from dependency on fossil fuels, mostly on oil, is very important. Therefore, support of electric vehicles belongs to these efforts. Governments and organizations are pushing through laws to increase numbers of cars consuming alternative fuels. Different countries are making different legislative steps to reach that. For example, there are countries where car manufacturers are obliged to produce given percentage of low-emission (or no-emission) cars or, on the other end of the market, owners of electric cars can often claim tax benefits.

Furthermore, ownership of electric car is fashion, in developed countries primarily. People which want to be environment-friendly are using cars with electric drive even though they are often more expensive. The price difference is often significant. Mainly due to the fact that electric cars are produced as luxury cars with lot of new technologies and unconventional appearance.

At the turn of the 20th century, electric drive for cars was not much developed, compared to conventional combustion engines, and thus brought us necessity for great amount of new technical solutions from many branches in order to design electric cars which are able to survive in that competitive automotive environment. Cars with sufficient horsepower, range and reliability – vital features that make car capable of being used everyday.

As technologies advanced, there are many cars with fully electric or combined (hybrid) drive which are more than comparable to cars with conventional engine nowadays. Electric vehicles market share is no longer negligible – overall numbers of EV are estimated to 740 000 in 2014 – but percentage is still low [1].

Electric cars made up less than half percent of the 85 million of new vehicles which were sold in the world in 2014. Leading country is Norway, where electric cars made up 1.6% of all running cars [1]. The chart above (Fig. 1) shows that the main boom started in 2011 and there is significant expansion every year.

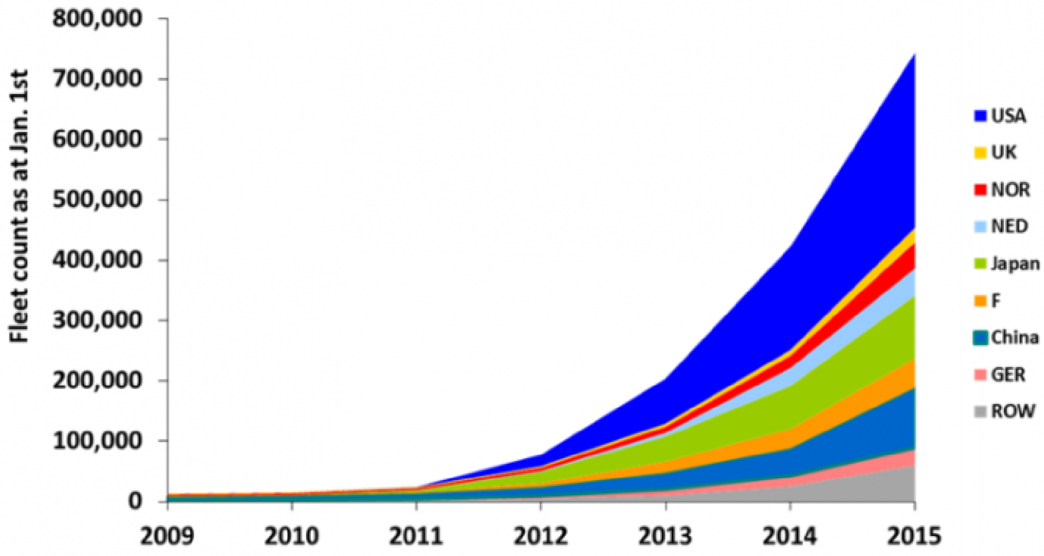

Fig. 1 – Number of electric passenger cars in the world *[1]*

Although they are suitable for every day use, there are issues modern electric cars have to face. Besides motor, those cars are full of electric appliances and systems which increase total power consumption and thus significantly reduce range. It leads to necessity of storing more and more energy inside the car. So here we come to the point.

This thesis is focused on technologies for storing electric energy in electric vehicles. Besides introduction, it is divided into four main parts. At first, there is examined inception of batteries and EVs. From the very beginning, how electricity was discovered, developing of early batteries and EVs expansion in early 1900s and subsequent huge decline of electric vehicles. The chapter continues by abstracting interesting electric vehicles and their basic parameters that were produced throughout foregone century. Special attention is given to their power supply and technologies they are equipped by. At the end of the first chapter, there is an overview of types of electric cars and general informations about situation in Europe and Czech Republic. Following chapter starts with list of basic terms related to batteries and continues with research of technologies that are or have been applied in electric cars cars. In the fourth chapter, we will have a look on technologies promising great progress, but which are still under the development. Besides batteries, there will also be analysed alternative technologies for storing electrical energy that might be used. There will be a summary at the end of this paper dealing with mentioned technologies and general difficulties.

2. HISTORY OF ELECTRO-MOBILITY

2.1 The beginning of electric energy storing

Although electric cars are very popular nowadays, their early predecessors were built in the middle of 19th century. Invention of the electric car is not attributed to one particular date or inventor. It took long time and many components discoveries preceded it. One of the most important component is indisputably a source of electric energy. It took a long way to develop device with parameters sufficient to supply appliance such as vehicle.

At the very beginning, there was discovery of the electricity itself. It happened by discovery of galvanism by Luigi Galvani in 1780 and subsequent invention of the first electrical battery on that basis. That was Volt's voltaic pile (Fig.2) i.e. series of copper and zinc discs separated by cloth or cardboard soaked in sodium chloride solution (salt water) built in 1800. This device was able to supply electric circuit by stable current, but capacity was very low. However, it was very contributive to study of electrochemical cells, electrical decomposition or isolation of the chemical elements.

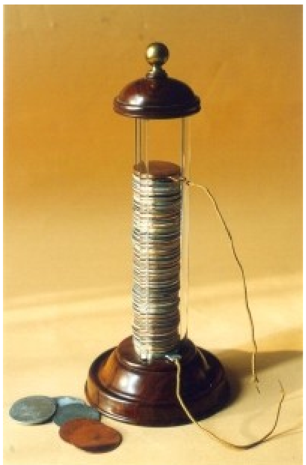

Fig. 2 – Voltaic pile [3]

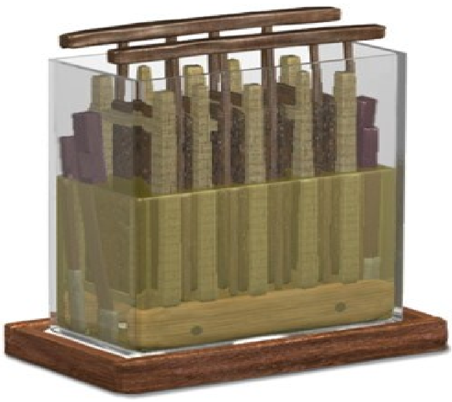

Fig. 3 – Planté's lead-acid battery [2]

The first rechargeable lead-acid battery was invented in 1854 by Wilhelm J. Sinsteden. Five years later, French physicist Gaston Planté improved these lead-acid cells (Fig. 3) to the point of commercial viability. His design had smooth lead plates separated by parchment and felt but his cell had to be recharged many times before a sufficient peroxide coating built up on the positive plate and reached usable capacity. Next significant improvement was carried out by Camille Alphonse Faure in 1881. He patented new method of coating lead plates, therefore, he tripled capacity of the original Planté's design and opened a way to industrial manufacture of lead-acid batteries.

2.2 Early electric vehicles

One of the first electric vehicles was tricycle (Fig. 4) modified by William Ayrton and John Perry in 1881. It has a top speed of 14 km/h and range almost 40 Km. The first model used open sulphuric-acid batteries. The power and so the speed was controlled by dipping lead plates into the acid. The more immersed led plates were, the higher current flew through their bigger surface. *[11]*

In 1891, William Morrison made the first electric vehicle with re-chargeable batteries and US market finally became interested. Their vehicle was able to carry 6 to 12 passengers with range of 80 kilometres. Subsequently, Morris & Salom as a company produced vehicle called Electrobat 1 (Fig. 5). It was capable of 24 km/h and its range was 80 to 160 km. Next model, Electrobat 2 was equipped by pneumatic tyres and controller. *[11]*

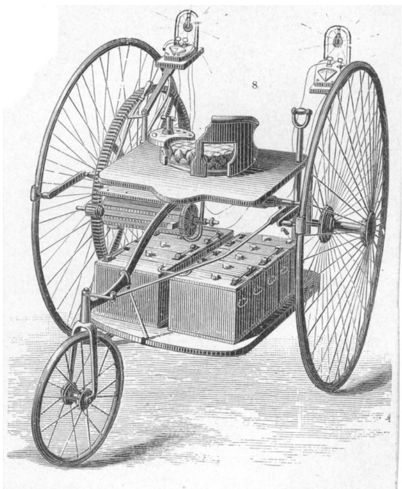

Fig. 4 – Ayrton and Perry tricycle [11]

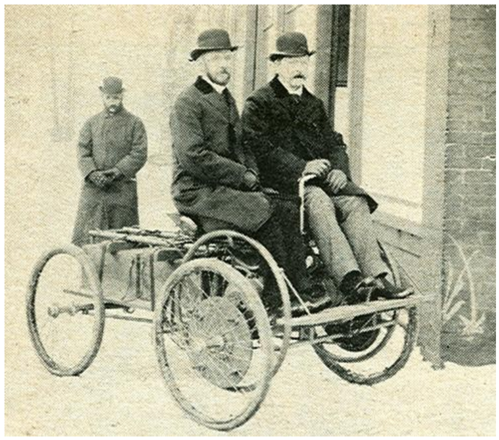

Fig. 5 – Electrobat 1[12]

In 1896, company Morris&Salom built Electric Road Wagon with rear wheels steering, two 1/2hp motors, 44 lead-acid cells and range of 50 kilometres. The car was designed for New York City taxis, but not only Morris&Salom was engaged in developing vehicles for taxi service. Walter C. Bersey designed a fleet of cabs for London. They were introduced in 1897 and soon after received a nickname “hummingbird” owing to light humming sound the made. The design of twelve hummingbirds included interchangeable battery pack that could be replaced in 2-3 minutes using a hydraulic lifting system so that the vehicle did not have to be put out of operation while charging. The battery made a significant portion of overall two tons of car weight. The New York City had also fleet of electric propulsion hansom cab taxis. This fleet was run by Samuel's Electric Carriage and Wagon Company and counted up to 62 cabs by the end of the century. *[11],[12]*

2.3 Heyday of electric vehicles in early 1900s

Electric cars were also used for breaking speed records in the time of their boom. One of the cars was La Jamais Contente driven by Camille Jenatzy who broke the barrier of 100km/h by setting the speed record of 105.8 km/h in 1899. His torpedo-shaped car was made of aluminium alloy, equipped by two 25kW electric motors with maximum current throughput of 125A. Electric energy was supplied by 200V lead-acid battery consisting of 100 cells, 2V each. *[11],[31]*

Fig. 6 – La Jamais Contente in museum [14]

Electric vehicles were very popular at those days. Compared to cars with gasoline motor, there was lack of vibrations, noise, and unpleasant exhausts' smell. In addition, combustion motor had to be started by manual crank which was difficult. Steam powered cars were common, but the start-up time was even up to 45 minutes in cold weather contrary to instant use of electric ones. Therefore, electric drive was often preferred by women. In some cases, electric cars were considered so strongly as women's car, that false radiators were mounted to them to appear like gasoline car.

Yet, in the 1900, there were 40% cars powered by steam, 38% by electricity (33,842 vehicles total) and 22% by gasoline in the USA. We can say it was heyday of electric cars. [6]

Thomas Edison, universal innovator and inventor, believed that electric cars are superior to the others but also felt the necessity of battery with better parameters than existing lead-acid. Therefore, he invested lot of time to improve Waldemar Jungner's idea of nickel-cadmium cell by substituting cadmium by iron. In 1901, he patented nickel-iron (NiFe) battery with significantly higher energy density and offered it to car manufacturers. In his disappointment, car industry rather adopted lead-acid battery because his design suffered of poor performance in low temperatures while being costly. In addition, not even his redesign from 1907 met success due to decline of electric cars production.

2.4 Dark age of electric vehicles

Following years were unfavourable for electric vehicles. Large crude oil reserves found in USA decreased price of gas. Electric starter became standard part of gasoline car, hence, uncomfortable starting by hand crank vanished. In 1913, Henry Ford established serial assembly-line production of his model T which was often three or four times cheaper than cars with electric drive. Developing infrastructure of roads and necessity of travelling long distances increased requirements for range, which meant just larger tank for cars with combustion engine but immense obstacle for electric vehicles since there were not technologies for storing sufficient amount of electrical energy on-board.[6]

Ensuing period of time meant significant decline, almost extinction, for electric cars. They were very rare and used in special purposes only or built by do-it-yourself guys. Special electric vehicles were used as forklifts or luggage trolleys or golf carts. In the streets, we could met quiet milk floats, especially in Great Britain where they are occasionally used up to now.

There were few manufacturers who tried to break through with small urban electric cars within the 20th century. For example, Henney Kilowatt was mini car based on Renault Daupine, released in 1959 in USA. The early model used lead-acid Exide 36V battery (eighteen 2V batteries) with range of 65km, later model used 72V battery (12 six-volt batteries) and was able to reach speed of 100km/h and its range was about 100km. This model used combined controller consisting of relays and diodes. [32]

Fig. 7 – 1970s electric milk float [12]

Fig. 8 – 1968 Amitron [13]

The AMC (American Motors Corporation) built few cars with electric propulsion system. Amitron was one of them. It was experimental compact car full of advanced technologies, built in 1967. The car used two lithium-nickel-fluoride batteries with total capacity of 22.5kWh in combination with nickel-cadmium (NiCd) battery. NiCd battery was there for covering power peaks during accelerating. In addition, Amitron was the first car that used regenerative breaking to increase the range of the car. Another full-electric car built by AMC was Rambler American in 1969. The battery pack contained 160 nickel-cadmium cells, each with the capacity of 75Ah. Use of advanced speed controller gave it decent acceleration, but there were still problems with range. Those cars never went to production. Even though their development ended in a stage of prototypes, they showed the possibilities for electric vehicles and advancement of technologies.

Speaking of electric vehicles, we must not forget the first manned vehicle driven on the Moon. The Lunar Roving Vehicle, first delivered on the Moon in 1971 during Apollo 15 (16 and 17 subsequently) mission. The rover was equipped by two 36-volt silver-zinc potassium hydroxide non-rechargeable batteries with 242Ah total capacity and range of 92km. [16]

Back to the Earth, between years 1974 and 1977, Sebring-Vanguard based on Florida produces pretty successful 2-seat CitiCar. They used 36V flooded lead-acid battery, later on 48V, and reached top speed of 40km/h, 55km/h respectively. Range of CitiCar was approximately 65km. There were 4,444 cars produced overall.[15]

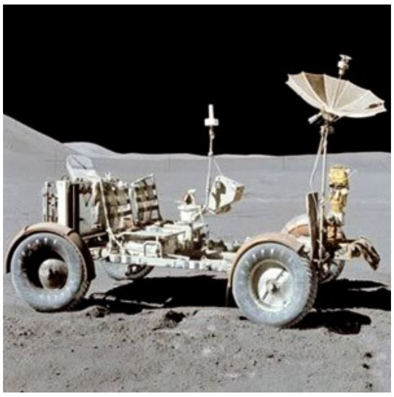

Fig. 9 – Lunar rover [16]

Fig. 10 – CitiCar in museum [17]

Those and lot of other types of EVs were designed or prototyped, but majority did not succeed against conventional cars. Technologies were neither developed enough to be affordable nor able to compete the market, therefore, they were often built as concepts and highlights of manufacturers’ technologies. This situation started to change at the end of the 20^{th} century.

2.5 Renewed interests in electric cars

Not only oil crisis renewed interests in electric vehicles. Governments around the world started to apply emission restrictions and cars were not forgotten. Great expansion of electric cars took place in late 1990s. Low-emission and no-emission cars started to be supported by different ways. Often, tax benefits were implemented for purchase and run of an electric car. Sometimes, car manufacturers were obliged to produce given portion of such a cars. In addition, fast technological development enabled to make electric cars approximate to cars with combustion engine in terms of space, horsepower, safety, reliability or affordability.

One of the first interesting program was started in 1996 by General Motors. They introduced 2 seat coupé called EV1. The first generation counted 660 vehicles, being produced until 1999. Three phase alternating current induction motor was controlled by IGBT power transistor and fed by lead-acid battery. This set up was characterized by 102kW output power and 110 to 160 kilometres of range. Since 1999, the battery was replaced by 60Ah and 312V battery pack Panasonic with the same chemistry, which slightly enhanced the range of EV1 in the second generation. Great advance was achieved when lead-acid was supersede by nickel-metal hydride battery pack with nominal voltage 343 Volts and 77 Ah. EV1 with new battery pack was able to travel 160-220 kilometres between charges. It took eight hours to charge the battery to 100%, tough the first 80% could be obtained in 1 to 3 hours. [18],[23]

With 1,117 cars produced, the EV1 program has ended in 2002. In view of the fact that cars were available only for lease, all cars were reclaimed and returned to GM’s possession. Company decided to destroy all cars, donating only about 40 cars with deactivated powertrains to museums or educational institutions. [18]

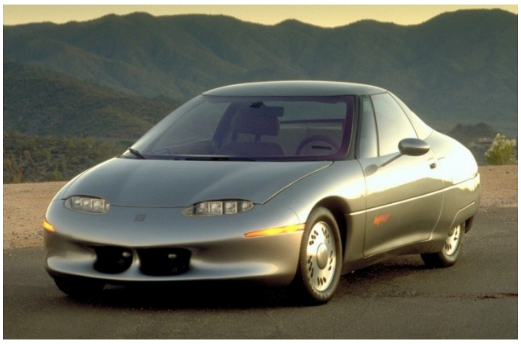

Fig. 11 – General Motors EV1 [18]

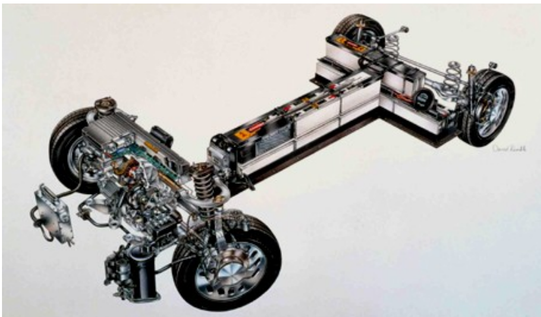

Fig. 12 – EV1 powertrain [23]

In 1997, Japanese Toyota started to lease the first generation of model RAV4 EV, popular compact SUV converted to electric propulsion system. The car was equipped by NiMH battery consisting of 24 twelve-volt packs storing 27 kWh of energy. Charging of battery fully depleted to fully charged took about five hours, while driving range was about 150 km. 50 kW electric motor was able to move the car by its maximum speed 126 km/h. Toyota offered this model until 2003 when production discontinued. [33]

The second generation followed not until 2012. Toyota equipped the car by advanced lithium-ion battery which was developed in collaboration with Tesla. 386 V battery pack consisted of 4,500 cells weights 380 kg with capacity 41 kWh. Despite higher capacity, driving range was not much better than the first generation's. Considering that car was heavier, bigger, equipped by more than twice as powerful motor and full of modern technologies that consume energy, it was great success. [34]

Back in 1997, the first mass-production hybrid car was introduced in Japan. It was Toyota Prius that has started successful career for its own and for other hybrid electric vehicles (HEVs). Combination of electric propulsion system and combustion engine enabled Prius to keep advantages of both technologies and made him one of the most successful hybrid car. According to Toyota, Prius reached more that 3,500,000 cumulative sales between 1997 and June 2015. [30]

Those early models showed that electric and hybrid cars are able compete conventional cars, and find its place on market. In last two decades, electric vehicles cut off immense market share. In the following chapter, we will have a look at current situation.

3. CURRENT ELECTRO-MOBILITY SITUATION

3.1 Types of electric vehicles and their representatives

3.1.1 Battery electric vehicle (BEV)

Often referred as full-electric. Those cars run entirely on electric energy stored in their battery pack. Battery is recharged by plugging to power grid or by energy recuperation that increases the range. The have no tailpipe emissions.[19]

The most advanced BEV is Tesla model S. This car was introduced in 2012. Till the end of 2015, there were 107,000 cars sold and Tesla plans add more 80-90 thousand of model S/X in 2016. According to the model specification, Tesla S has range 260-528 km and maximum motor power 285-568 kW that makes model S very agile. Battery type is analysed later. The price is corresponding to the level of equipment. The basic model may be bought for $76,000, the most powerful and fully equipped model's price is more than $140,000.[20],[21]

In contrast, Nissan Leaf belongs to compact cars. In 2015, cumulative sales exceeded 200,000. Leaf has 80kW motor, 24kWh Lithium Manganese Oxide battery and the price starts at $30,000. With the range about 170km, Leaf is more confident in cities and suburbs. [22]

3.1.2 Hybrid electric vehicle (HEV)

The HEVs incorporate internal combustion engine (ICE) and electric battery, control and motor. Electric powertrain is used as a supplement to ICE and car can operate in three modes: engine powered (electric motor is used only for regeneration of energy and charging batteries by regenerative breaking, works as an generator in this mode), full electric drive (usually up to given speed and/or maximum range about 5-30 km), or combined (electric motor may deliver its power in low revolutions of ICE and benefit the propulsion by its low-rpm torque or it may increase total horsepower, in case of rapid acceleration or high speed). HEVs are not able to be charged directly from power grid, they just benefit from collecting energy that is usually wasted in form of heat (e.g. breaking) and storing it for later use. This system makes car fuel-efficient and low-emission while benefits of ICE are kept. That is why HEV are so popular among electric vehicles nowadays.

One of the most successful HEV is indisputably Toyota Prius with more than 3,500,000 sold cars worldwide, while all Toyota hybrid models combined make more than 8 million sells. [19],[30]

3.1.3 Plug-in hybrid electric vehicle (PHEV)

As the name suggest, PHEVs are hybrid electric vehicles with possibility of being charged from power grid. Usually, they are equipped by larger battery than HEV in order to maximize the benefit of plug-in charging. Size of the battery can not be comparable with battery from BEV due to its significant weight, therefore, manufacturers have to find compromise between electric range and weight of a car. The full-electric range is up to 50km, but usually, it is a half.

PHEVs are able to go further distances in full electric and combined mode than HEVs, their increasing popularity in last few years is proven by increasing number of PHEV models. Plug-in hybrids do not have to be only small or compact cars. The most sold PHEV in Europe in 2014 and 2015 is Mitsubishi Outlander P-HEV, SUV which weight is 1.85 tons. It is equipped by 2.0l gasoline engine, two 60kW electric motors and 12kWh lithium-ion battery pack capable of delivering range of 52km in all-electric mode.[35]

Leader of global sales is Chevrolet Volt. Manufactured by General Motors, this car was sold under different brands as Chevrolet Volt, Holden Volt, Vauxhall Ampera and Opel Ampera. Combined sales of those siblings reached 100,000 in 2015. [19]

3.2 Electric vehicles in Czech Republic

Czech republic is not widely known as big fan of electric vehicles. There are many reasons why, starting at low density of population, it means small urban areas, therefore most of electric vehicles are not suitable to our land. Although, electro-mobiles are no longer designated for cities and infrastructure is being built, number of charging points increases every year. According to ChargeMap.com , there are 153 charging points, with total 369 sockets. Charging points are denser in bigger cities, but we can say that they are distributed all over the country. [36]

1. 1. 2016 in the Czech republic, there are 2440 electric vehicles, but only 790 passenger cars, nearly 1500 electric motorbikes, 59 lorries and 81 special machines. The most popular are: Nissan Leaf (120), BMW i3 (105), Tesla Model S (104) and Volkswagen e-Golf with Volkswagen e-Up! (154). [37]

4. CURRENT TECHNOLOGIES

4.1 Basic terms

Before examining technologies used nowadays, we are going to go through basic terminology and explanation.

Batteries are usually marked with Nominal voltage. It is given by voltage of cell type and their number, if connected to series in order to get higher voltage. On the other hand, when cell voltage drops to Cut-off voltage, it is considered as fully discharged.

Capacity represents amount of energy stored inside the battery. In other words, load current delivered over time. Ah (Ampere-hour) is unit of capacity. The larger the capacity is, more time to full charge is required.

Not only capacity affects time of charging. For particular battery types, we are allowed to use just very specific current, otherwise the cell may be destroyed. C-rate specifies the speed of charging and discharging and is related to Ah rating. 1C means that battery may be charged and discharged by the current corresponding to Ah capacity value, therefore the battery is charged in one hour. 0.5C halves the current and doubles the time of charging and vice versa for 2C.[4]

Charge efficiency tells us, how many percent of the energy that we charged to battery we can take back.

Specific energy defines battery capacity in weight (Wh/kg) and energy density reflects relation between capacity and volume (Wh/l). They specify amount of energy stored per unit of mass and volume, respectively. Whereas specific power (W) gives us the power the battery is able to deliver at given time.

We may also use terms as; energy/consumer price - shows price of 1Wh, self-discharge rate – percent of total capacity loss per month, cycle durability – how many charge and discharge cycles is battery able to operate before fails to meet specific performance criteria, depth-of-discharge – amount of total capacity that has been discharged expressed in percent.[5]

4.2 Lead-acid batteries

Lead-acid batteries are the first rechargeable batteries, invented in mid 1800s. Still, more than 150 years later, it is widely used type of battery. Despite the fact, that lead-acid provides very low energy-to-weight and energy-to-volume ratio, it compensates for high surge currents and low cost.

It went through many enhancement, but the basic principle is still the same. There are two porous lead (Pb) plates where one of them is covered by lead oxide (PbO_2). They are immersed into 35% (may vary) sulphuric acid (H_2SO_4). When discharged, sulphuric acid reacts with lead and lead oxide and combines into lead sulphate ($PbSO_4$)on both electrodes and the electrolyte is depleted of sulphuric acid (became pure water - H_2O). This reaction is expressed by following equation:

$$PbO_2 + 2\,H_2SO_4 + Pb \leftarrow\rightarrow PbSO_4 + H_2O + PbSO_4 \qquad (2.1)$$

There is variety of lead-acid batteries. Besides usual flooded batteries (FLA), where electrolyte is poured directly into cell, there are sealed lead-acid or valve-regulated lead-acid (VRLA) batteries, e.g. absorbed glass mat (AGM) and gell cells – electrolyte is soaked into absorbent material. They can be operated in any physical orientation without leakage unlike usual flooded batteries. *[5]*

Tab. 1 – Basic parameters of lead-acid batteries [5]

Specific energy	30-40 Wh/Kg
Energy density	60-75 Wh/l
Specific power	180 W/kg
Charge/discharge efficiency	50-92%
Eregy/consumer price	7-18 Wh/$
Self-discharge rate	3-20%/month
Cycle durability	500-800 cycles
Nominal voltage, cutoff voltage	2.1V, 1.75V

The most known lead-acid battery is an ordinary car SLI battery. SLI stands for starting, lighting and ignition. They are designed to deliver a lot of energy in short time, but drain out only about 5% of its capacity, before charged back up to maximum from an alternator. They are not suitable for electric car drive because deep discharge damages electrodes and decreases maximum capacity and life span of battery. But they are used in electric cars in common way: to supply 12V electric appliance in the car, being charged by DC-DC converter from the main battery pack.

There are special lead-acid batteries for power supply of drive called deep-cycle batteries, also know as traction batteries. They can be discharged to 20% of its capacity and charged again without objection.

The lead-acid deep-cycle batteries are made with different parameters and use, as well as industrial batteries designed for stationary use (to store large amounts of energy) or industrial batteries that are designed to be moved (for forklifts, floor sweepers) but those are very heavy to be used in electric cars.[4]

Instead, there are batteries designed to be relatively lightweight, in comparison with industrial ones mentioned above, with sufficient capacity and cycle durability. Those batteries are widely used in EVs (golf carts, electric wheelchairs) because of the price, nevertheless the battery pack is significant (25-50%) portion of the vehicle weight due to the technology limitations and low specific energy.[4]

4.3 Nickel-based batteries

4.3.1 Nickel-iron

Nickel-iron battery (NiFe) was invented in 1899 by Waldemar Jungner, later improved and patented by Thomas Edison who hoped that his battery would be used in electric vehicles for SLI. Combination of iron anode with nickel oxide-hydroxide cathode gives nominal voltage 1.2V. Charging requires 1.6-1.7V. NiFe is resilient to overcharge and discharge as well as to vibrations and high temperatures. Unfortunately, this battery performed poorly in low temperatures and its weight was also enormous. But its advantages makes NiFe very durable (20-50 years, occasionally even 100 years old battery still works), even though they did not found its use in electric vehicles, they were suitable for stationary applications as forklifts or rail-road signalization or household power backup.[28]

Electrochemistry[28]:

cathode: $$2\,NiOOH + 2\,H_2O + 2\,e^- \leftrightarrow 2\,Ni(OH)_2 + 2\,OH^- \tag{3.1.1}$$

anode: $$Fe + 2\,OH^- \leftrightarrow Fe(OH)_2 + 2\,e^- \tag{3.1.2}$$

4.3.2 Nickel-zinc

Another nickel based battery which was patented at the beginning of the 20th century. NiZn rechargeable battery was used in rail cars between 1932 and 1948, easily recycled, but suffered from high self-discharge and short life cycle. Enhanced electrolyte chemistry reduced this problem and NiZn became attractive chemistry. It found its use in high-drain applications. [29]

Electrochemistry[29]:

$$2\,H_2O+Zn+2\,NiOOH \leftrightarrow Zn(OH)_2+2Ni(OH)_2 \qquad (3.2.1)$$

4.3.3 Nickel-cadmium

Nickel-cadmium (NiCd) batteries in sealed form were preferred for many years for two-way radios, emergency medical equipment, professional video cameras and power tools. In its beginning, NiCd battery manufacturers tried to promote their new chemistry as superior to existing lead-acid. Long shelf live (can be stored in discharged state), good low temperature performance, possibility of ultra-fast charging and low cost made those batteries widely used. Nowadays, NiCd is being abandoned due to the toxicity of cadmium.[4],[26]

Electrochemistry[28]:

cathode: $$NiOOH+H_2O+e^- \leftrightarrow Ni(OH)_2+OH^- \qquad (3.3.1)$$

anode: $$Cd+2OH \leftrightarrow Cd(OH)_2+2e^- \qquad (3.3.2)$$

4.3.4 Nickel-metal hydride

Batteries combining nickel with hydride alloy (NiMH) are one of the most used rechargeable batteries nowadays. Battery manufacturers, such as Panasonic, Energizer and Duracell offer durable and low-cost NiMH in AA and AAA sizes. NiMH has almost twice the capacity of standard NiCd with the absence of toxic metals. They are environmentally friendly, and nickel content makes their recycling profitable. As disadvantage we can count high self-discharge. Modifying the hydride materials may lower the self-discharge but it also reduce the specific energy. Batteries for the electric powertrain rather use modification to achieve robustness and prolong a life span. Toyota as a market leader in 2012 have been selling mostly NiMH battery pack in their cars. 2013 all-electric Prius and RAV4 started to use lithium-ion. [4]

Electrochemistry[28]:

cathode: $$NiOOH+H_2O+e^- \leftrightarrow Ni(OH)_2+OH^- \qquad (3.4.1)$$

anode: $$MH+OH^- \leftrightarrow M+H_2O+e^- \qquad (3.4.2)$$

4.4 Lithium batteries

4.4.1 Lithium-ion

Lithium-ion batteries (LIB) belong to the family of batteries widely used in consumer electronics for its high energy density and low self discharge. LIBs are growing in popularity for military, electric vehicles and aerospace application. Current electric cars are equipped almost only by LIB. There are many types of LIB with various features.

Tab. 2 – Basic parameters of lithium-ion batteries [5]

Specific energy	100-265 Wh/Kg
Energy density	250-676 Wh/l
Specific power	250-340 W/kg
Charge/discharge efficiency	80-90%
Eregy/consumer price	2.5 Wh/US$
Self-discharge rate	8-30%/month
Cycle durability	400-1200 cycles
Nominal voltage	3.2-3.7V

Generally, Lithium-ion battery uses a metal oxide (and other additives) as cathode and porous carbon as anode. During discharge, ions flow from the anode to the cathode through the electrolyte and separator. When charging, ions flow the opposite direction (Fig.4). Basic Lithium-ion cell may be enhanced by adding variety of active materials in order to obtain better/different parameters.[5]

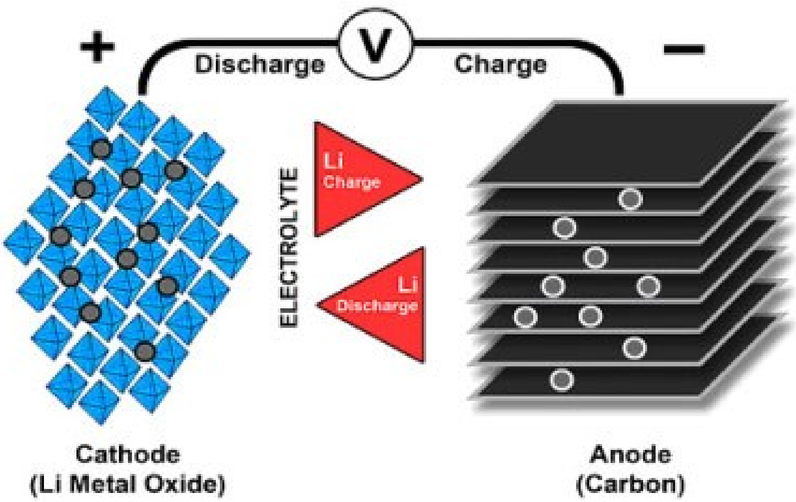

Fig.13 – Basic principle of lithium-ion batteries[4]

Lithium Cobalt Oxide ($LiCoO_2$) batteries are popular in cellphones, laptops or digital cameras. They have very high specific energy and great performance but, due to their limited specific power, short lifespan and poor safety, they are not suitable for use in electric cars. Besides, pure cobalt is very expensive.

Electrochemistry:

cathode: $LiCoO_2 \leftrightarrow Li_{1-x}CoO\,2 + xLi^+$ (4.4.1)

anode: $C + xLi^+ \leftrightarrow Li_x C$ (4.4.2)

Lithium Manganese Oxide ($LiMn_2O_4$) has three dimensional architecture that improves ions flow on the electrode. That decreases internal resistance and improves current handling. It means high thermal stability and enhanced safety, but capacity is roughly one-third lower than Li-cobalt. Moreover, Li-manganese allows engineers to optimize the battery design either for lifespan, specific power or specific energy. It is used in power tools, medical devices and electric power-trains.[4]

Electrochemistry:

cathode: $Li_{1-x}Mn_2O_4 + xLi^+ xe^- \leftrightarrow LiMn_2O_4$ (4.4.3)

anode: $Li_x C_6 \leftrightarrow xLi^+ + xe^- + C_6$ (4.4.4)

Lithium Nickel Manganese Cobalt Oxide ($LiNiMnCoO_2$) or NMC is trending technology that leading battery manufacturers are focusing on. Combining those three metals enhances each other strengths. They are evenly distributed in cathode compound 1/3-1/3-1/3. This battery is preferred candidate for the electric vehicle due to its high capacity, high power, long life span and thermal stability. It is used in e-bikes, EVs, medical devices and as industrial batteries.

Lithium Nickel Cobalt Aluminium Oxide ($LiNiCoAlO_2$) or NCA offers high specific energy and reasonably good specific power with long life span. These parameters made Elon Musk choose NCA for EV's manufactured by Tesla, despite a higher price and below-average safety. Model S is equipped by battery pack containing 7104 NCA cells in 16 modules with high level of computer control. Battery weights 1200kg and total capacity is 85 kWh. The first battery of this kind appeared in 1999.[8]

Lithium Titanate ($Li_4Ti_5O_{12}$) also referred as LTO are known since 1980s. They were long time under development, the first practical use came in 2008. Contrary to the other lithium systems, there is lower terminal voltage on cell (2.4V), lower specific energy and the battery is still expensive. On the other hand there are big advantages. Battery can be charged up to 5C (typical charge rate for other lithium-based systems is 1C), discharge rate may be up to 10C (even up to 30C in 5 second pulses), therefore great specification for traction battery. Very long live span, excellent performance and superior safety makes this battery suitable for UPS and powertrain (Mitsubishi I-MiEV, Honda Fit EV). [4]

4.4.2 Lithium-ion polymer battery

LIP, LiPo, Li-polymere refers to lithium-ion battery with polymer electrolyte, but the chemistry is still on the same basis. LIP cells in pouch format are currently investigated to power electric vehicles. It is possible to use large number of cells to obtain required capacity, but some manufacturers are looking for large-format LIP cells. It may simplify connections between cells as their number drops, but safety of cells is not so good and lowers with larger cells.

Hyundai Motor Company uses LIP batteries in some of their hybrid vehicles and Kia Motors in electric Kia Soul.[7]

In the picture below(Fig 5), we can see comparison of Specific energy of selected technologies.

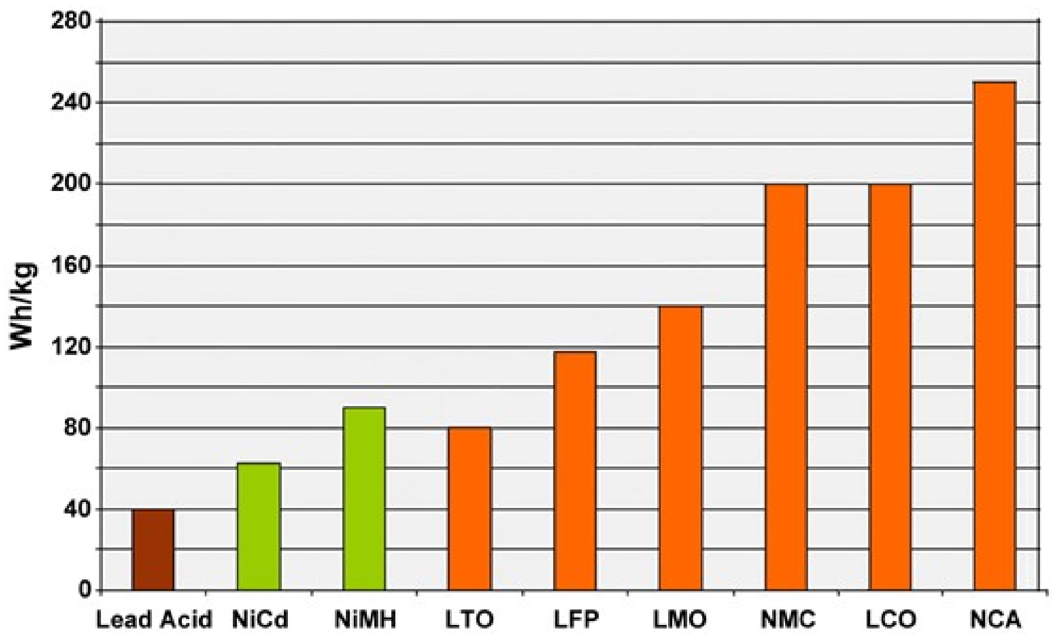

Fig. 14 – Specific energy of various battery cell technologies [4]

4.5 Fuel cells

4.5.1 Proton Exchange Membrane Fuel Cell

A PEM Fuel cell is an electrochemical device that consumes hydrogen fuel and oxygen and produces the electricity, heat and pure water. There are no harmful emissions.

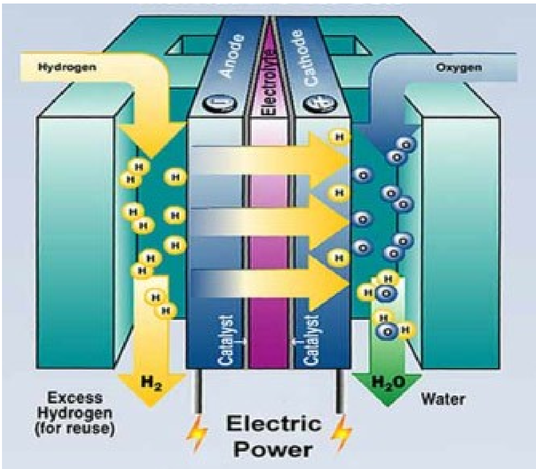

Fig. 15 -Principle of hydrogen-oxygen fuel cell[4]

Fundamentally, this fuel cell is reversed electrolysis. There are two electrodes separated by an electrolyte in the core (stack). The negative electrode (anode) receives the hydrogen and the positive electrode (cathode) collects the oxygen. Catalyst layer separates the hydrogen into positive hydrogen ions and electrons. They compound together with negative oxygen ions, forming water. Those particles move between electrodes generates electric charge and therefore the electric energy (Fig. 6). The only by-product is a water. Under load, fuel cell produces 0.6-0.8V.[4],[25]

Electrochemistry[25]:

cathode: $$\frac{1}{2}O_2+2H^++2e^-\rightarrow H_2O \qquad (5.1.1)$$

anode: $$H_2\rightarrow 2H^++2e^- \qquad (5.1.2)$$

total PEMFC reaction: $$H_2+\frac{1}{2}O_2+2e^-\rightarrow H_2O \qquad (5.1.3)$$

Electrochemical technology is twice as efficient as energy generated by combustion of hydrogen and oxygen, two inlet elements. They are plentiful on the Earth, and there are no CO2 emissions, unlike the gasoline powered systems. But there is a catch in it. The hydrogen is mostly bound to a substance and gas extraction is inefficient and energy consuming process. Efficiency is very low, some even says, that the hydrogen is nearly energy neutral. It means that it takes as much energy while produced as it delivers at the end device. Therefore, it might not be used as source of energy, but as medium for storing or transporting energy, similar to electric energy.

The hydrogen can be also produced with a reformer. In other words, extracted from an existing fuel such as methanol, propane, butane or natural gas. But there is some leftover carbon released.

The benefit of using fuel cell in cars is questionable. There is no pollution and high efficiency at the end, but it starts with consuming lot of energy previously gained by burning fossil fuels, expensive and difficult storage in robust metal tanks under very high pressure and necessity of a fuel transportation that also generates pollution. [4]

4.5.2 Alkaline Fuel Cell

Alkaline Fuel Cell (FEC) is preferred technology for aerospace, including the space shuttles. NASA chose Alkaline cell to produce the electric energy and drinking water for astronauts. Manufacturing cost are low, water management is simple and does not need compressors or other peripherals. AFC is larger in physical size and requires pure oxygen and hydrogen. Carbon dioxide present in polluted air may even damage the stack. Therefore, this technology, is not suitable for passenger cars drive. [4]

4.5.3 Solid Oxide Fuel Cell

Solid Oxide Fuel Cell has received renewed attention because of breakthrough in materials and operating temperature has been decreased from 800-1,000 °C to 500-600 °C that allows use of common materials in design rather than special ceramic parts in former design. Solid oxide or ceramic electrolyte may be used in this type. But still, requirement of such a high temperature exclude use in electric vehicles. It is suitable for medium and large power generation because of high efficiency (by-product is steam that may be lately used in steam generator and thus, efficiency is getting close to 60%). [4]

4.5.4 Molten Carbonate Fuel Cell

MCFC has high efficiency, is flexible to fuel, but requires operational temperature 600-700 °C and has a long startup. It is therefore suitable for large power generation, not for EVs. [4]

4.5.5 Direct Methanol Fuel Cell (DMFC)

Direct Methanol Fuel Cell is type of PEMFC. It is fed by methanol-water mixture (CH_3OH + H_2O). It is well developed in small scale, because manufacturers are adjusting DMFC to use in portable device. It has specific energy comparable with NiCd batteries.

Fig. 16 – Toshiba fuel cell with refuelling tank containing 99.5% methanol [4]

This system is simple, compact, requires no compressors, but low efficiency, complex stack and slow response make it unsuitable for EVs' drive. Waste products are carbon dioxide and water. In addition, methanol is highly poisonous and there are strict law restrictions for the market. [4], [25]

Electrochemistry[25]:

cathode: $$1\frac{1}{2}O_2+6H^++6e^-\rightarrow 3H_2O \tag{5.5.1}$$

anode: $$CH_3OH+H_2O\rightarrow CO_2+6H^++6e^- \tag{5.5.2}$$

total reaction: $$CH_3OH+1\frac{1}{2}O_2\rightarrow CO_2+2H_2O \tag{5.5.3}$$

5. FUTURE TECHNOLOGIES

5.1 Flow cell batteries

A flow battery is an electrochemical device that is a cross between traditional battery and fuel cell. Liquid electrolytes are mechanically pumped to core that consists of two electrodes separated by a membrane (Fig. 8) The membrane is a special foil that allows ions exchange between the electrodes but no electrolyte mixing. Ongoing ions exchange generates a charge on electrodes.[4]

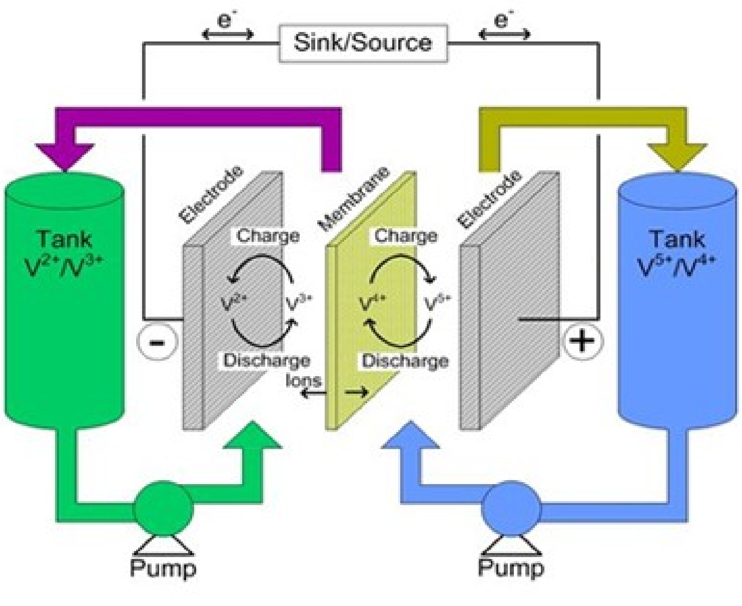

Fig. 17 – Principle of flow cell battery [4]

Most commercial flow batteries use sulphuric acid with vanadium salt as electrolyte because of its low corrosion. The vanadium is mined mainly in China, Russia and South Africa. Other flow batteries may contain precious metals as platinum, but research is continuing to find low cost and readily available materials. Liquid electrolytes are positively and negatively charged, so we refer them as catholyte and anolyte. [4]

Electrochemistry[24]:

catholyte: $VO^{2+}+H_2O-e \leftrightarrow VO_2^{+}+2H^{+}+e^{+}$ (5.1.1)

anolyte: $V^{3+}+e \leftrightarrow V^{2+}$ (5.1.2)

total reaction: $VO^{2+}+H_2O+V^{3+} \leftrightarrow VO^{2+}+2H^{+}+V^{2+}$

$$2VOSO_4+2H_2O+V_2(SO_4)_3 \leftrightarrow (VO_2)_2SO_4+2H_2SO_4+2VSO_4 \quad (5.1.1)$$

The Flow batteries perform best at size above 20 kWh, therefore as a bulk energy storage device. Each cell produces 1.15-1.55V, according to the chemical compound used. The specific energy is low compared to the other battery technologies and the power density is just moderate. It do not makes them much suitable for use in electric vehicles, but there is one great advantage contrary to other battery systems. Since the electrolytes are stored in tanks, there is simple way how to increase capacity – bigger tank. And in matter of charging – such a car not need to stay connected to a charger. We can instantly change the whole electrolyte volume in time no longer than casual gas tank refill. Used electrolyte might be charged again, therefore there would not be necessity of fuel transportation. [4]

5.2 Supercapacitors

Supercapacitors, sometimes referred as ultracapacitors, are electrochemical capacitors that bridge the gap between electrolytic capacitors and rechargeable batteries. They can store 10 to 100 times more energy per volume or mas than electrolytic capacitors and have much higher specific power than rechargeable batteries. Moreover, they have many times higher cycle durability (1 million). The problem is, they are circa 10 times bigger than conventional batteries for the same charge due to lower specific energy (1 to 30 kWh/kg). In addition, voltage of supercapacitor linearly decreases while discharged, it means just limited usable power spectrum.

Nevertheless, advantages of supercapacitors are giving hope to became superior power storage even for electric cars, even though they are not yet. Main advantages are: rapid recharge (1 to 10s), live cycle and specific power mentioned above, wide operating temperature range (-40 to 65 °C).

Application in electric powertrains is limited nowadays. They are used as peak-load enhancer for hybrid cars and vehicles with regenerative breaking where is need to rapidly absorb energy or cover peak power. [4]

5.3 Technologies in early stage of development

5.3.1 Lithium-sulphur batteries (LiS)

Both elements of this combination are light weight, therefore specific energy of LiS battery approaches 550 Wh/kg. It was achieved also by new electrodes design. Contrary to Li-ion where graphite anode hosted lithium ions, in LiS, graphite is replaced by lithium metal serving as electrode and supplier of ions. Cathode also lost some weight when metal oxide was replaced by lighter and cheaper sulphur. More direct donating and accepting ions also enhanced specific power up to 2,500 W/kg. Those qualities makes Lithium-sulphur batteries superior for use in electric vehicles. Unfortunately, this technology is not developed enough to practical use nowadays. There are issues with conductivity, degradation of sulphur cathode and poor stability at higher temperatures. It decreases cycle durability to bare 40-50 cycles.

Stanford engineers have experimented with adding nanowires, also enhancement with graphene done great results. [4]

5.3.2 Lithium-ion with silicone anode

Research showed, that silicon, among other anode materials, can store (theoretically) 10 times more, but it emerged that applying this finding would be challenge for researchers. There were promising attempts, but the silicone swells its volume three times when fully charged. And this swelling eventually breaks the electrical contacts within the material. So researchers have focused on maintaining conductivity.

The new silicon-anode design lay in a special flexible polymer that is conductive and able to bind closely to the silicon particles even as they change their volume. This technology is low-cost and compatible with standard lithium-ion batteries manufacturing. However, those efforts did not count with severe material reducing on the anode side, which transforms conducting polymers into insulator.[10]

In praxis, solving this issue by developing suitable polymer, or finding different solution, capacity of Li-ion batteries would significantly increased. Therefore electric vehicles would be able to go longer distances and supply more on-board appliance.[9]

6. CONCLUSION

In this bachelors thesis, I have got acquainted with the historical development of technologies that were used in electric vehicles since the discovery of electricity. I have followed the steps of inventions that led to the birth of electric vehicles, researched those early predecessors of modern electric cars and found many car manufacturers who tried to produce vehicles with electric propulsion, nevertheless technologies were not mature. I have also mentioned situation in Czech Republic. In the second half of my thesis, there are analysed the most used technologies for storing of electrical energy in electric vehicles through history and in present. Even though some types are surpassed, there is variety of battery technologies, which development continues ceaselessly and energy density, therefore range of electric car will probably rise manifold. Redox batteries, fuel cells and supercapacitors are another possible devices for storing electric energy that might gave slightly different direction in development.

I have indicated possible trends of future development of technologies. It may happen by progress in battery technologies we know, by development new types (e.g. Li-S or Li-air) or by inventing completely new ways of energy storage. Some currently known technologies just need to be slightly adjusted in order to meet requirements for mass production. Some of them may be researched for another few decades, similarly as it was with lithium-based batteries, which are known since 1970s but their application came not long ago. Development of the batteries goes hand in hand with expansion of electric vehicles and vice versa.

Despite the fact that electric cars are very popular and modern machines with very advanced technologies with no tailpipe pollution, they consume energy which must be generated elsewhere. Unfortunately, electric energy is not generated by clean and renewable sources with a few exceptions. Therefore, electric cars do not eliminate air pollution, they just move the burden to the remote power plants.

Considering just technological advancement, usability, affordability and popularity among people, electric cars would have great future, but we have to take account of other problems.

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